SEQUESTERING CARBON DIOXIDE WHILE PRODUCING NATURAL GAS

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CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/430,961 filed December 4, 2002.

FIELD OF THE INVENTION

This environmental-quality invention is in the field of apparatus and methods for sequestering greenhouse gases while producing natural gas from natural gas hydrates in a subterranean formation. The invention enhances the quality of the environment of mankind by contributing to the control of greenhouse gases.

BACKGROUND OF THE INVENTION

Hydrates are solid crystalline compounds, commonly known as clathrates. These crystalline compounds are formed of a "cage like" structure of water surrounding other molecules which are often gases (for example, methane, carbon dioxide) and whose structure is dependent on the size of the contained molecule. A thorough description of hydrates is contained in E. D. Sloan, Jr., *Clathrate Hydrates of Natural Gases*, Dekker N.Y. (1990). Natural gas hydrates are those hydrates formed from gases found in natural gas reservoirs. Natural gas hydrates have many properties similar to ice.

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Several models and descriptions of the occurrence of natural gas hydrates have been put forward in the literature and depend on the following factors: (a) the phase stability of the hydrate in terms of pressure and temperature; (b) the nature of occurrence of the natural gas hydrate in clastic sediments (for example, either clay or sand rich sediments); and, (c) the occurrence of the natural gas hydrate above or below ice-bearing permafrost, or the occurrence in marine-continental shelf or arctic-permafrost settings.

The discussion of recovering hydrates with respect to the present invention focuses on moderate to low clay content clastics that bear hydrates in a subterranean formation (either in arctic-permafrost or marine-continental shelf locations) where the hydrates are trapped in pores (of the clay or sand particles) that are of sufficient size after hydrate and/or ice dissociation as to provide permeability sufficient for production in a timely manner. In all likelihood, the best hydrate zones would be those below ice-bearing permafrost due to the added impact of ice dissociation on the overall energy requirements for production.

In the scientific literature, no model is put forward to explain how the hydrates occupy the pore space in the clastics. However, if the hydrates occupy a significant volume of the pore space they will reduce the permeability by several orders of magnitude. After hydrate dissociation, these previously hydrate-filled pores will improve heat transfer from convective flow through the reservoir and provide expanded heat transfer via conductive heat into the subterranean formation.

The pressure and temperature ranges for natural gas hydrate stability depends on the gas that is trapped in the hydrate. FIGURES 4A-4F show the stability ranges for two gases: methane and carbon dioxide. Methane is the most commonly occurring gas in natural gas hydrate deposits and in most places is greater than 98 mole % of the natural gas hydrate found.

Several methods of producing natural gas from hydrates have been suggested for clastic deposits:

1. Thermal stimulation
   (a) Steam, hot gas, hot water, and hot brine

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(b) In place combustion, electrical, radio wave or microwave heating

2. Depressurization
3. Hydrate inhibitor injection
4. Combinations of depressurization and thermal simulation

Also several enhancement methods such as fracturing or drilling with jet pumps have been suggested, or selecting a formation with a free gas zone. Free gas zones exist at the base of many hydrate bearing zones and provide a pathway for flow when the gas hydrate dissociates.

Hydrates of natural gas occur where the temperature and pressure ranges are appropriate for their stability and the occurrence of natural gas exists. Hydrates are both biogenic and thermogenic. Biogenic hydrates are derived from biological activity. Many of the biogenic hydrates exist where biological activity in the past has produced methane gas and this gas has been in many different manners moved into the hydrate phase stability window. Thermogenic hydrates are derived from the thermal response through geologic time of burial of carbon rich sediments and subsequent hydrocarbon production. Thermogenic hydrates are associated with major hydrocarbon occurrences where the natural gases similar to the biogenic gases have been moved into the hydrate phase stability window.

The phase stability window for the ice-like crystalline solid in hydrate exists in two primary locations: regions with permafrost and regions on the continental shelf. The occurrence of hydrate in these regions is enhanced in areas where thermogenic gases available from deeper hydrocarbon deposits have migrated into the stability range, for example, the North Slope of Alaska or the Gulf of Mexico.

The estimates of hydrates as resource usually include estimates of all occurrences of the resources including the resource where it is probably not developable due to association with sediments high in clay content. The hydrate cores in the Mallik well in the McKenzie Delta, Canada showed that significant resources exists in low to moderate clay clastic formations that can be approached with similar technology used in hydrocarbon recovery.

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Key gases believed to have greenhouse gas effects are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). These gases are naturally occurring and make up less than one tenth of one percent of the gases in the atmosphere. The atmosphere consists mainly of nitrogen at 78 percent and oxygen at 21 percent. Greenhouse gases are believed to trap heat in the atmosphere and without them it has been estimated that the earth's surface would be significantly colder than it is today. Concern exists that the further release of greenhouse gases will cause a further increase in atmospheric temperature.

In the past, major concern has focused on the emission of carbon dioxide from burning coal, oil, and natural gas. Recently the release of methane to the atmosphere has come under scrutiny and concern. Methane gas may have significantly more impact than carbon dioxide gas on the atmosphere. Estimates in the literature suggest methane has a 12-20% greater efficiency for the proposed greenhouse gas phenomena.

Numerous authors have suggested that hydrate deposits may be accessible to future release of greenhouse gases. It has been suggested that the geologic record provides evidence that potentially large volumes of greenhouse gases in the past, in particular methane, have been released into the atmosphere because of sea level changes and that these changes impacted the global temperature. While those past changes are not those potentially brought on by man, they nonetheless suggest that global atmospheric changes may have taken place because of methane hydrate dissociation. The fear is that current dissociation of methane hydrate, which is a more efficient greenhouse gas, will accelerate the supposed rate of warming.

Since methane hydrates provide a very clean source of energy, they may provide the most environmentally acceptable pathway to non-oil hydrocarbon energy. It may also be beneficial to remove the methane from these hydrate deposits and replace it with carbon dioxide irrespective of whether it is man or nature causing the period of warming that many scientists have suggested.

DESCRIPTION OF PRIOR ART

The sequestration of carbon dioxide in aquifers has been described in patents such as U.S. Patent No. 5,397,553 to Spencer and U.S. Patent No. 5,261,490 to Ebinuma et al. In the injection or production of natural gases in wells that pass through the temperature and pressure regime where hydrates are stable and exist (where the hydrocarbons are in an immobile form), several production techniques have been patented and discussed in the literature. Some of the patents in this area are U.S. Patent No. 5,950,732 to Agee et al.; U.S. Patent No. 5,713,416 to Chatterji et al.; U.S. Patent No. 4,007,787 to Cottle; U.S. Patent No. 5,261,490 to Ebinuma et al.; U.S. Patent No. 4,424,858 to Elliot et al.; U.S. Patent No. 4,376,462 to Elliot et al.; U.S. Patent No. 4,262,747 to Elliot et al.; and U.S. Patent No. 3,920,072 to Kern.

Heretofore in the production of natural gas through permafrost or intervals with pressure and temperature regime where hydrates exists, the zone would have to be insulated, refrigerated, or the like. Thawing of the permafrost is to be avoided as well casing collapse is then an issue to be addressed. Some of the patents in this area are U.S. Patent No. 5,816,325 to Hytken; JP10317869A2 to Kazuyuki; U.S. Patent No. 5,291,956 to Mueller et al.; U.S. Patent No. 4,595,057 to Deming et al.; U.S. Patent No. 4,399,867 to Wolcott; U.S. Patent No. 3,220,470 to Balch; and U.S. Patent No. 2,148,717 to Whitney.

Proposed methods and apparatus for the capture of carbon dioxide to remove carbon dioxide as a greenhouse gas have been much discussed in the literature and many techniques exist. For example, DOE/EIA-0573 (2000) *Emissions of Greenhouse Gases in the United States 2000*, November 2001; S. Kim et al., *Potential for Advanced Carbon Capture and Sequestration Technologies in a Climate Constrained World*, Battelle Pacific Northwest National Laboratory (PNNL) – 13095 (Feb. 2000). Removal of carbon dioxide from natural gas has been around for years and is a mature technology.

The various sources of carbon dioxide gas in the present invention require the carbon dioxide to be in a gas, such as found in produced natural gas, in effluent from the combustion of oxygen and hydrocarbons, in effluent from fuel cell chemical reactions that convert hydrocarbons to electricity, or in effluent from a gas to liquid process.

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However, no active method for the sequestration of carbon dioxide into hydrate bearing subterranean zones exists.

S. Kim et al., cited above, state that:

"The present state of carbon capture and sequestration technology is focused on the capture of carbon dioxide (CO_2) from the flue gas of fossil-fuel electric power plants and the disposal of the captured CO_2 in various geological formations. Great attention has been placed recently on the technology for CO_2 capture from stationary power plants, and several technologies exist today to capture CO_2 from flue gases. Capturing CO_2 from power plants is not a new idea and has its origins as sources of CO_2 for enhanced oil recovery and for agricultural CO_2 fertilization in greenhouse applications."

"According to Herzog et al. [H. Herzog et al., *$C0_2$ Sequestration: Opportunities and Challenges*, Massachusetts Institute of Technology, Cambridge, MA (1999)], the current cost of CO_2 capture from coal and natural gas power plants is 66 to 282 dollars per tonne of carbon ($/tC) avoided depending on the specific type of power plant. The additional capital, fuel, operations, and maintenance costs of CO_2 capture add 1 to 3 cents per kWhr to the electricity cost of base plants. Part of the cost of CO_2 capture is due to energy requirements of the capture process that result in net power losses. Such energy penalties can range from 13 to 37 percent depending on the plant type. Current capture technologies, however, can remove 75 to 90 percent of the CO_2 emitted from the combustion of fossil fuels. . . ."

"Current demonstration of CO_2 sequestration for the sole purpose of combating climate change lies with Statoil, a Norwegian oil company. Induced by a Norwegian carbon tax of 50 dollars per tonne of CO_2 (183 $/tC), the first commercial CO_2 capture and sequestration facility started operation in September 1996 by Statoil. CO_2 from a natural gas field is sequestered into a sandstone aquifer one kilometer beneath the North Sea. The CO_2 is injected from a floating rig at a rate of 20,000 tonnes per week which corresponds to the rate of CO_2 produced from a 140 MWe coal-fired power plant."

"According to Herzog, the cost of Statoil's sequestration operation alone is 15 dollars per tonne of CO2 (55 $/tC). Other than the experiences discussed above, there are

no large scale commercial carbon capture and sequestration technologies currently deployed."

"Combining the above capture costs and Statoil's sequestration cost, the total cost of CO_2 capture and sequestration ranges from 121 to 337 \$/tC. Unless there are carbon control policies like the Norwegian carbon tax, such high CO_2 capture and sequestration costs are not likely to provide incentives for the deployment of these technologies."

Similarly, the methods and apparatus proposed for the production of hydrates from subterranean formations are many (Sarish L. Patil, "Overview of Gas Hydrate Production Technology", May 23, 2002, SPE-AAPG Western Region Meeting, Anchorage, Alaska; D. Khairkhah et. al., "The Production potential of the Mallik field reservoir", *Geologic Society of Canada Bulletin* 544, 1999, pp. 377-399; E. D. Sloan, Jr. "Clathrate Hydrates of Natural Gases" 2nd Edition revised and expanded, 1998, pp. 513-537). Much documentation exists concerning the many workable and unworkable schemes for the production of hydrates and at the same time the applicable practice of the art of hydrocarbon recovery is widespread. However, no active production technique exists for the production of hydrocarbons from hydrates in subterranean zones. The Messoyakha field in the West Siberian Basin of the former Soviet Union has been speculated to have produced from hydrates which exist above a free gas level, but the data is ambiguous.

Despite all of these mature technologies, the art of sequestering carbon dioxide and the art of producing hydrates have not been undertaken jointly.

SUMMARY OF THE INVENTION

In a broad aspect, the invention is a method of sequestering carbon dioxide and producing natural gas including: (a) injecting an injectant containing at least some amount of carbon dioxide into a zone containing natural gas hydrates; (b) releasing natural gas from the hydrates by allowing thermal transfer and pressure changes from the injectant to the hydrates; and (c) sequestering the carbon dioxide in the zone that previously contained the natural gas hydrates.

One embodiment of the invention is a method of sequestering carbon dioxide while at the same time producing natural gas. This embodiment includes: (1) drilling and

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completing at least one well in a subterranean formation where there is at least some natural gas in the form of natural gas hydrate; (2) supplying an injectant stream of a desired composition containing at least some carbon dioxide; (3) pumping the injectant into the well to the appropriate depth and at a controlled temperature and pressure; (4) circulating the injectant to the natural gas hydrate to cause dissociation of the natural gas hydrate to release free natural gas vapor; (5) collecting the evolved natural gas and transporting it to the surface; and (6) allowing at least part of the carbon dioxide to be sequestered in the subsurface location.

The present invention, by combining the processes of methane production and sequestration of carbon dioxide, will make the cost of sequestration of carbon dioxide and the cost of hydrate production become competitive. Gravity/density segregation of the liquid injectant (containing carbon dioxide) from the methane gas produced from in-situ hydrate dissociation allows production of methane and entrapment of the liquid carbon dioxide injectant. The temperature and pressure conditions that form a solid clathrate from the injectant containing the carbon dioxide are reached by a change in pressure through production or injection by allowing reassertion of the regional temperature profile. Thus, the carbon dioxide is sequestered.

The process includes:

1. Drilling and completing at least one well into a subterranean formation where there is at least some natural gas in the form of hydrate;

2. Supplying gas/injectant from the gas injectant supply subsystem to be injected into the well at the appropriate depth and at the controlled temperature and pressure and composition;

3. Controlling and monitoring the gas/injectant supply subsystem, the well subsystem, and the subsurface containment subsystem to provide for the initiation, continuation, or shutdown of injection and production;

4. Injecting the injectant within the subsurface containment subsystem as a liquid so that heat transfer from the injectant is highly efficient, and so that the pressure change and the rate of dissociation of natural gas hydrate in place allows the natural gas hydrate to dissociate to free natural gas as a vapor and to migrate via gravity/density

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segregation (while being constrained by the subsurface containment subsystem) to a production well or wells; an injection pressure that is above the fracture pressure is allowed if the fractures formed do not breach the subsurface containment subsystem; and

5. Producing the hydrate-evolved natural gas that has migrated to the production well while allowing gravity/density segregation of the hydrate-evolved natural gas from the injectant so that the injectant containing carbon dioxide (all or in part) remains in the subsurface containment subsystem where, after the final production stages, the pressure and temperature are allowed to reduce to where the injectant can change phase to a hydrate; the produced natural gas is sent to the production facility or the produced natural gas is recycled (all or in part) with the gas supplied for injection from the gas/injectant supply subsystem. The natural gas may be further processed for removal of water and separation of methane and carbon dioxide before being supplied to the gas/injectant supply subsystem or the production facility.

Another embodiment of the invention is a system for sequestering carbon dioxide and producing natural gas from a subterranean natural gas hydrate by means of a controlled injection of an injectant stream that contains at least in part carbon dioxide. This injectant stream is cycled/injected into a subterranean formation that underlies either ocean or land. The system includes: (a) a gas supply subsystem for preparation and injection of the injectant stream into a well; (b) a well subsystem for delivering the injectant into the subsurface formation and for producing the resultant natural gas; (c) a subsurface containment subsystem including a subsurface formation with static and dynamic permeability variations that form permeability barriers to the circulation of gas and liquids; and, (d) a monitoring and control subsystem for maintaining the production process and for controlling the injection and production pressure and temperature suitable for the desired outcome of methane production and carbon dioxide capture and sequestration in the subsurface formation.

BRIEF DESCRIPTION OF THE DRAWINGS

The preferred and alternative embodiments of the present invention are described in detail below with reference to the following drawings.

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FIGURE 1 is a schematic representation of a generic system that embodies the invention.

FIGURE 2 is a schematic representation of a more specific embodiment of the invention.

FIGURE 3 is a schematic representation of a magnified view of a melting natural gas hydrate formation in a subterranean location.

FIGURE 4A is a phase diagram where the composition of the injectant in an arctic-permafrost well bore is 100 mole % carbon dioxide. The diagram displays the resultant phases.

FIGURE 4B is a phase diagram where the composition of the injectant in an arctic- permafrost well bore is 50 mole % carbon dioxide and 50 mole % methane. The diagram displays the resultant phases.

FIGURE 4C is a phase diagram where the composition of the injectant in an arctic- permafrost well bore is 10 mole % carbon dioxide and 90 mole % methane. The diagram displays the resultant phases.

FIGURE 4D is a phase diagram where the composition of the injectant in a continental shelf well bore is 100 mole % carbon dioxide. The diagram displays the resultant phases.

FIGURE 4E is a phase diagram where the composition of the injectant in a continental shelf well bore is 50 mole % carbon dioxide and 50 mole % methane. The diagram displays the resultant phases.

FIGURE 4F is a phase diagram where the composition of the injectant in a continental shelf well bore is 10 mole % carbon dioxide and 90 mole % methane. The diagram displays the resultant phases.

FIGURE 5A is a phase diagram showing the phase relationships that exist for an injectant (containing only about 13 mole % carbon dioxide) formed directly from the Prudhoe Bay Unit gas cap. Thus, FIGURE 5A is a phase diagram where the composition of the injectant is 75.02 mole % methane, 7.95 mole % ethane, 3.99 mole % propane, and 13.04 mole % carbon dioxide. This is the natural composition of the gas cap that exists in the Prudhoe Bay Unit.

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FIGURE 5B is a phase diagram where the composition of the injectant is 43.13 mole % methane, 4.57 mole % ethane, 2.29 mole % propane, and 50.00 mole % carbon dioxide. This is the Prudhoe Bay Unit gas cap composition with sufficient added carbon dioxide to increase the carbon dioxide content to 50.00 mole %.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

One goal of this invention is to provide a process for producing natural gas that combines a method of production of natural gas from hydrates and a method of sequestration of carbon dioxide in a subsurface location. Currently the need to remove greenhouse gases from the atmosphere has been emphasized in the Kyoto Protocol and in the United States by the Clear Skies Initiative by U.S. President George W. Bush.

There are many valid reasons for reducing carbon dioxide in the environment. Also, it can be readily seen that carbon dioxide present in a methane-rich natural gas acts as a diluent which contributes no energy and increases the volume of the gas which must be handled or processed. This in turn leads to increase in size and cost of the equipment in the plant utilizing the natural gas and in the cost of development of the pipeline. The carbon dioxide reduces the heat value of natural gas.

Hydrates are a major clean hydrocarbon resource. No production exists from this resource because of the economics associated with production. Hydrates require energy to be produced because of the need to dissociate methane from the solid crystalline structure of the methane hydrate. Net energy production is possible from hydrates. At least 1/10 of the methane from hydrates is expected to be used in the energy requirements for the dissociation and subsequent production. Because of the energy requirements for production, the costs were non-competitive before the present invention.

Costs for production of natural gas are affected by the requirements for removal of carbon dioxide. In natural gas, the BTU value of the gas is reduced by the presence of carbon dioxide. For example, a natural gas reservoir may contain, for example, 12 vol. % carbon dioxide. Several technologies exist for removal of the carbon dioxide from the natural gas before shipment. Often in the past, the carbon dioxide that was removed was vented to the atmosphere. Cost estimates for removal of carbon dioxide from natural gas is in the range of $50 per ton of carbon.

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Current U.S. Department of Energy (DOE) cost estimates, cited by H. Herzog et al., *CO_2 Sequestration: Opportunities and Challenges*, Massachusetts Institute of Technology, Cambridge, MA (1999), suggest the removal of carbon dioxide from power plants has a cost range of $66 to $282 per ton of carbon depending on the specific type of power plant. Future power plants may reduce these costs to $10 per ton of carbon. New fuel cell technology may even further reduce the cost. These current costs of carbon dioxide capture add 1 to 3 cents per kWhr to the electricity cost of base plants. These energy penalties range from 13 to 37 percent depending on the power plant type. Current capture technologies can remove 75 to 90 percent of the carbon dioxide emitted from the combustion of fossil fuels. Once the carbon dioxide is removed, the question is where to sequester it.

The current capture technologies as applied to carbon dioxide disposal in the practice of injecting carbon dioxide into oil wells to enhance recovery are mature and are used to provide information on costs of carbon dioxide disposal. However, storage of the carbon dioxide for long periods of time has not been evaluated. Because of industry carbon taxes or credits, future gas industry production is expected to focus on commercial capture of carbon dioxide.

In the present invention, the recovery of natural gas from hydrates focuses on the moderate to low clay content clastics that bear hydrates in subterranean formations, either in an arctic-permafrost location or in a marine continental shelf location, where the hydrates are a solid phase in pores of sufficient size such that after hydrate and ice dissociation, the pore system provides permeability of sufficient extent for convective and conductive heat transfer and/or depressurization of the in-place hydrate and production of the resultant gas in a timely manner. (The resultant gas may not be 100% methane, but may contain other gases such as carbon dioxide.) Thus, it should be understood that the present invention is a process that can use either thermal methods or depressurization, or both thermal methods and depressurization.

It should also be noted that the solid phase of natural gas hydrates in the pores in the subsurface containment subsystem allows a dynamic pressure seal that changes location with time as hydrate is melted and then along with a sealing shale layer above

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the hydrate zone forms a dynamic containment system which allows the injectant in the hydrate zone to remain in the liquid phase. Production of the hydrate-dissociated gas allows little mixing with the injectant and the injectant to retain its liquid phase.

The Generic System Shown in FIGURE 1

A generic system that embodies the present invention is illustrated by the system 10 shown in FIGURE 1 which includes several subsystems: (a) a gas/injectant supply subsystem 12 that provides the gas/injectant; (b) a well subsystem 52 that connects the gas/injectant supply subsystem to the in-place subterranean source of natural gas hydrates and that pipes the gas produced up to the surface; (c) a subsurface containment subsystem 66 that provides gravity/density segregation of the liquid injectant which contains carbon dioxide, dissociation of the in-place methane hydrate, production of gas, and recycling of the injectant/gas provided by well subsystem 52 from gas supply subsystem 12; and, (d) a control and monitoring subsystem 77 that provides monitoring and control of the pressure, temperature, and composition and flow of the injectant gas and the produced gases.

Gas/Injectant Supply Subsystem

The gas/injectant supply subsystem 12 in FIGURE 1 employs one or more possible sources of the gas 34 used for the injectant 56. For example, source 24 is a natural gas accumulation. Another example is source 26 which is the exhaust of a fossil fuel power generation plant. Another example is source 28 which is the exhaust of a fossil fuel compressor plant. Another example is source 30 which is the exhaust from a gas-to-liquids plant.

The injectant 56 is more efficient for heat transfer if the injectant is a liquid at the zone where it is being injected. More importantly, if the injectant is a liquid it allows gravity/density separation of the liquid carbon dioxide injectant from the hydrate-evolved natural gas.

FIGURES 4A-F are pressure and temperature diagrams that show:

1. The phase diagram and envelope (lines 260, 312, 360, 408, 460, and 512) of an injectant where the injectant is of the specified composition, the phases of the

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injectant that have a liquid phase or critical phase and are shaded for three conditions where methane vapor exists:

(a) The liquid and vapor phase of the injectant co-exist and the injectant has a density greater than the vapor released upon dissociation of the hydrate (areas 300 and 504);

(b) The liquid phase of the injectant exists (that is, there is no vapor phase of the injectant) or the critical phase of the injectant exists and the injectant has a density greater than the vapor released upon dissociation of the hydrate and the pressure is below the fracture pressure gradient (areas 252, 302, 402, 452, and 502); and

(c) The pressure is above the fracture pressure gradient (areas 250, 304, 348, 400, 450, and 500).

2. The phase envelope (lines 258, 310, 358, 410, 458, and 510) for 100% methane. For this phase envelope, the hydrate phase is in the higher pressure and lower temperature region and the vapor phase is in either the lower pressure or higher temperature regions. The typical composition of an in-place hydrate is near 100% methane.

3. The specific pressure and temperature profile of a well (lines 256, 308, 356, 406, 456, and 508) within the area of hydrate occurrence. This is the pressure and temperature profile for each well. The intersection of the well bore pressure and temperature gradient (lines 256, 308, 356, 406, 456, and 508) with the methane phase envelope (lines 258, 310, 358, 410, 458, and 512) shows where the in-place hydrates are stable and can exist in the subsurface location.

4. The fracture gradient for the well (lines 254, 306, 354, 404, 454, and 506) is the injection pressure which, if exceeded, will fracture the formation. The fracture pressure of a well, where hydrates are stable, depends upon the depth of the hydrates. The maximum fracture pressure is based upon the maximum depth of the hydrate occurrence. Fractures can breach the subsurface containment and cause pressure leakoff. Vertical fractures can leak off to low pressure zones. Whether vertical fractures occur is dependent on local stress conditions or perhaps other unknown factors. Horizontal fractures may even help the production process.

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5. The ocean floor (lines 412, 462, and 514).

For the pressure and temperature profiles for the arctic-permafrost setting, a pressure gradient of 0.421 psi/ft and a fracture gradient of 0.695 psi/ft was used. For the pressure gradient for the marine-continental shelf setting, a pressure gradient of 0.45 psi/ft and a fracture gradient of 0.695 psi/ft were used. Temperature gradients were taken from T.S. Collett et al., "Natural Gas Hydrates", SPE-AAPG Western Region Meeting, May 23, 2002, Anchorage, Alaska. Fracture gradients, well bore pressures, and temperature gradients are dependent on the conditions specific to the location of the well.

It should be noted that if the injectant is above the critical point, the injectant is a single phase. For pure carbon dioxide, a temperature of 87.87° F, a pressure of 1071 psia, and a volume 0.0342 cu ft/lbm is the critical point (see Robert S. Metcalf, Petroleum Engineer's Handbook, Table 20.2 Some Physical Constants of Hydrocarbons). (The unit "lbm" refers to pounds of mass.)

At conditions such as these, the injectant has the characteristics of a single phase. This critical phase can be used as a liquid injectant if the density is greater than the vapor released from the hydrate at subsurface conditions. Phase and density data specific to the injectant and to the in-place hydrate composition where this invention is to be used should be obtained from laboratory analyses to ensure that the appropriate relationships between pressure, temperature, and density for the injectant are used in the inventive system.

FIGURES 4A-F display several injectant compositions (containing different amounts of CO_2 and methane) where the injectant 56 contains at least some carbon dioxide. The shaded areas that are designated as shaded areas 250 and 252 in FIGURE 4A; shaded areas 300, 302, and 304 in FIGURE 4B; shaded areas 348, in FIGURE 4C; shaded areas 400 and 402 in FIGURE 4D; shaded areas 450 and 452 in FIGURE 4E; and shaded areas 500, 502, and 504 in FIGURE 4F show the pressures and temperatures where the liquid phase or critical phase of the injectant 56 is stable and the vapor phase of the hydrate 100 (in FIGURE 1) is stable and the injectant at subsurface conditions has a density greater than the density of the vapor phase released by the dissociation of the hydrate. The injectant 56 needs to be a liquid and to be denser than

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the vapor phase released during hydrate dissociation for the desired gravity/density partitioning to take place.

The optimal pressures and temperatures are designated as shaded area 252 in FIGURE 4A, shaded area 302 in FIGURE 4B, shaded area 402 in FIGURE 4D, shaded area 452 in FIGURE 4E, and shaded area 502 in FIGURE 4F.

The effects of injection pressure on formation fracturing in the subsurface containment subsystem will need to be evaluated on an individual well basis. The stability zone for hydrate occurrence and its exact pressure profile in the subsurface along with the pressure range under which fracturing will occur in the orientation of the fractures in this zone and its effects on the injection containment may further constrain the range of optimal pressure and temperature of the injectant. The shaded areas designated as shaded area 304 in FIGURE 4B, shaded area 348 in FIGURE 4C, shaded area 400 in FIGURE 4D, shaded area 450 in FIGURE 4E, and shaded area 500 in FIGURE 4F are at pressures that are above the fracture pressure of the rock formation containing the hydrate as well as the fracture pressure of the overlying shale. Injection at pressures greater than the fracture pressure can breach the subsurface containment. The stress fields at the time of injection are critical to the orientation of the fracture (vertical or horizontal). A horizontal fracture does not pose a problem. A vertical fracture that fractures the overlying shale may be a problem because of the migration of gas along that fracture and potential subsequent breach of containment and depressurization of injectant.

The shaded areas designated as area 300 in FIGURE 4B and area 504 in FIGURE 4F are not effective at partitioning the evolved natural gas from the hydrate because of the injectant vapor which is present in these pressure and temperature ranges.

In FIGURE 1, source 24 is a natural gas accumulation (that is typically not from a hydrate source) that supplies produced gases 16 to conduit 14. Because this source of gas may not contain enough carbon dioxide to form a liquid injectant at subsurface conditions, additional carbon dioxide may be added to injectant 56 to ensure this. This additional carbon dioxide is added during gas conditioning in module 36.

In many areas, a natural gas accumulation rich in carbon dioxide exists at deeper depths than where the methane rich hydrates exist. An example of this source 24 is the

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natural gas accumulation in the Prudhoe Bay Reservoir, Alaska, where the natural gas accumulation is beneath the hydrate zone known as the Eileen Hydrate Accumulation. This natural gas accumulation is called the Prudhoe Bay Unit (PBU) gas cap and it contains approximately 13 mole % carbon dioxide. Thus, the supply of carbon dioxide for source 24 in subsystem 12 could come directly from a well connected to a deeper gas source and carbon dioxide from the deeper gas source could be produced to the surface and then be injected into the hydrate zone. Additional carbon dioxide will be required to be added to the gas from the natural gas source so that its composition as an injectant is liquid at the pressure and temperature for the production of the hydrate. Carbon dioxide removed from the gas cap by gas processing can be used for injection or it can be mixed with the gas cap gas to form a gas of suitable composition for an injectant.

Source 26 is a fossil fuel electric power generation plant which produces exhaust gas 18 containing carbon dioxide from the engine of the generation plant. Source 28 is a fossil fuel compressor plant which produces exhaust gas 20 containing carbon dioxide from the engine of the compressor plant. Current engine technologies produce exhaust gases containing from 3-12 volume % carbon dioxide and significantly more NO_X. Power plant technologies currently being developed, such as solid oxide fuel cells and molten carbonate fuel cells, reduce the NO_X emissions and provide a flue gas primarily composed of carbon dioxide. Thus, solid oxide fuel cells and molten carbonate fuel cells are possible sources of injectant 34. This gas may need minimal gas handling or compositional modification before being supplied for injection.

Current NO_X production from a power or compressor plant can be injected into hydrates as a hot gas, but not as a liquid. The cost of removing NO_X from flue gas drives up the cost of production and may make the process too expensive. Utilizing the injectant as a liquid, so that density/gravity segregation occurs, is the preferred mode of operating the present invention. Thus, the gas/injectant stream 34 should be a liquid injectant, containing at least some carbon dioxide, that is injected into the subsurface containment subsystem 66.

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Exhaust gas 22 is from natural gas-to-liquids plant source 30. The exhaust gas contains some carbon dioxide. This carbon dioxide would be used in the gas source 34 and may require processing in module 36.

Thus, the gas/injectant stream 34 should form a liquid injectant, containing at least some carbon dioxide, that is injected into the subsurface containment subsystem 66. The injectants with the higher carbon dioxide content allow a broader range of options for using the injectant. If the content of carbon dioxide is high enough, as in FIGURES 4A and 4B, the injectant can be liquid at a pressure and temperature range below the well bore stability of hydrate. This allows depressurization to be utilized for the production of the hydrate evolved gas.

The gas/source 34 is pumped through conduit 14 in FIGURE 1. In the case of source 24, where the gas supply (a natural gas reservoir) is underneath the hydrate accumulation, the well injection casing string may be the conduit. Otherwise, conduit 14 will be on the surface supplying the exhaust gases or produced gases to initial gas processing module 36. The gas processing module 36 performs gas processing functions such as expansion or compression, temperature control, water removal, and/or composition adjustment using conventional technology.

The gas storage module 38 in FIGURE 1 is located before the final gas processing injection module 40. The gas storage module 38 is either (a) a tank on the surface; or (b) a reservoir that is the source of the subsurface natural gas accumulation used in source 24. The final gas processing module 40 provides temperature and pressure control prior to injection and includes gas compressors, gas pumps, gas expansion chambers, gas heaters and/or heat exchangers.

On the upstream side of FIGURE 1, produced gas processing module 42 is on the surface and separates the produced gases, such as methane and carbon dioxide so that additional removed carbon dioxide 44 can be sent to storage module 38 to be injected, and/or methane can be removed prior to further gas processing and distribution at the production facility 48. Some of the methane 32 from production facility 48 flows through pipe 76 as needed to fuel the power generation plant 26, to fuel the compressor plant 28, and/or to supply the gas-to-liquids plant 30. The remaining methane from

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production facility 48 is transported through pipe 96 to a natural gas distribution system. Gas processing modules 36, 40, and 42 may be part of the production facility 48 and may contain common elements.

Well Subsystem

The well subsystem 52 includes the injection pipe string 54, the production pipe string 58, a larger well bore 60, injection packer 62, and production packer 64. The well subsystem can consist of one or multiple wells.

The final injectant 56 flows down the injection pipe string 54 and is discharged where the natural gas hydrates are located. The natural gas 94 which is released from the hydrates flows up the production pipe string 58 to the gas processing module 42.

The well subsystem 52 is created by drilling and completing at least one well in a subterranean formation where there is at least some natural gas in the form of hydrate. The site is chosen where the geologic formation and hydrate occurrence allows for a subsurface containment subsystem 66.

FIGURE 1 shows the larger well bore 60 which can be lined with conventional casing or not as desired and which is drilled into a subterranean formation so that well bore 60 penetrates a zone of hydrate. Various effects need to be considered in the design of the well, for example, effects such as: (a) melting of the surrounding well bore hydrate and/or ice/permafrost by heat transfer from the injectant or casing-cement heat of formation; (b) casing strain and stress effects via changes in pore pressure because of different subterranean rock properties affecting ice or hydrate stability; and, (c) the formation of hydrates in the production and injection strings, especially in times of shut down. The well should include the necessary precautions to remedy these effects. These remedies include insulated tubing and casing, hydrate formation prevention techniques such as heating using heat tape, hydrate inhibitors, cement selection, and selection of slip joints as are conventional in the industry.

Boreholes are drilled at the desired distances and patterning from the surface into the subterranean formation. Thereafter the casing and pipe strings are set into the formation to the desired depth. Perforated or slotted casing is employed at the lower end of well bore 60 as shown in FIGURE 1. The injection string 54 is placed so that injection

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occurs at greater pressure and is placed deeper than the production string. The system is designed to promote circulation between the injection and production string so that convective and conductive heat transfer and depressurization are optimized. The system may be employed in a horizontal well so long as the injection string is located so that the natural gas migrates into the production string via pressure differences. Since the system relies on gravity segregation, the injection string should penetrate deeper than the production string.

Subsurface Containment Subsystem

The subsurface containment subsystem 66 in FIGURE 1 is illustrated in a three-dimensional schematic representation. It includes natural geologic containment structure 68 comprised of a layer of shale 98 and the in-situ solid (unmelted) natural gas hydrates 100. The size of the zone where the hydrates have melted within geologic containment structure 68 will increase over time. It should be understood that the clastic grains still remain in the zone where the hydrates have melted. For example, at time T1 the zone within the geologic containment structure will be of size 70; at time T2 the zone within the geologic containment structure will be of size 72; and at time T3 the zone within the geologic containment structure will be of size 74. Thus, this dynamic containment structure 68 will be defined through time by subsurface and injection conditions as the hydrate dissociation increases with time.

Injection packer 64 is placed in the lower portion of well bore 60 to block injectant 56 from production string 58. Production packer 62 is placed higher in well bore 60 to block production gas 94 from going up inside well bore 60 and to insure that production gas 94 goes up production pipe string 58. In a typical well, drilling will go through a layer of shale 98 which will function as the ultimate top of the subsurface containment subsystem 66. The containment shale 98 provides a vertical seal for the produced gas evolved from the hydrates underlying the containment shale.

Thus, the selection of the formation of the subsurface containment system is critical. It is selected so that an overlying lithologic-permeability barrier isolates the hydrate zone below and so that the permeability barrier will not be significantly affected by melting of the hydrate. The overlying lithologic-permeability barrier should be of

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sufficient lateral and vertical extent to allow the gas/liquid circulation system to operate and the pressure and temperature to be maintained for the liquid injectant.

Dissociation of the natural gas hydrate occurs by emplacement of the injectant 56 within the subsurface containment subsystem 66 by using heat transfer from the injectant, pressure change by pressure draw down on the production string, and by the rate of dissociation of natural gas hydrate to allow the natural gas hydrate to dissociate to free natural gas and to migrate to the production string 58. The methane hydrate dissociates to water and methane in a ratio of about 8:1.

If the injectant 56 is injected at a high enough pressure, fractures in the subsurface rock formation will occur. The shaded areas designated as area 250 in FIGURE 4A, area 304 in FIGURE 4B, area 348 in FIGURE 4C, area 400 in FIGURE 4D, area 450 in FIGURE 4E, and area 500 in FIGURE 4F are at pressures that are above the fracture pressure of the rock, which will possibly result in breaching the subsurface containment. The effects of injection pressure on the formation fracturing on the subsurface containment will need to be evaluated on an individual well basis. The stability zone for hydrate occurrence and its exact pressure profile in the subsurface, along with the pressure range under which fracturing will occur such that it affects subsurface containment in this zone, may further constrain these optimal pressure and temperature regions.

If the principal stress fields and other unknown factors are such that these fractures are parallel to the bedding and to the containment shale barrier at the top of the interval, there may not be a problem with breaching the subsurface containment subsystem. However no matter what the type of fracture, vertical or horizontal (or parallel to the bedding), the injectant should not be injected at a high enough pressure to cause the subsurface containment system to be breached by a fracture that would cause insufficient pressure retention in the subsurface containment subsystem for the injectant to exist as a liquid phase. For example, if the injectant 56 or the hydrate-evolved natural gas 94 exhibits pressure leak-off because a vertical fracture penetrated the sealing shale at the top of the subsurface containment subsystem, then the injectant may depressurize and

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become vapor or the vapor phase derived from the hydrate will not reach the production string because of gas migration along the fractures.

A free gas zone often exists below a stable hydrate zone. Emplacement of the injectant in this zone may not be possible because dynamic subsurface containment cannot be maintained. Increasing the pressure in this zone is dependent on the size of the aquifer underlying the free gas zone and chances are that the zone will be limited to pressure increase. If this free gas zone is encountered, it is recommended to produce the gas to the surface by decreasing pressure and to depressurize the well so that hydrate production occurs. Care should be taken that the injectant remains a liquid at these reduced pressures.

If the injectant can be injected at a lower pressure, the injectant can be injected at and sequestered at the narrow pressure and temperature range that exists between the injectant phase envelope and the hydrate phase envelope. In FIGURE 4A, for example, the carbon dioxide will form a hydrate and methane from the hydrate will be in a vapor phase. This will allow continued production of methane while carbon dioxide is at the range of temperature and pressure where it can form a solid hydrate.

As discussed above, the narrow range of temperature and pressures that define the difference between the injectant phase envelope and the methane phase envelope could be used as a range of temperature and pressure in the subsurface to abandon the well. The temperature and pressure of the subsurface can be controlled by the rate of injection and the temperature of injection, regional temperature gradient, the rate of dissociation, phase transition temperature changes, and by pressure drawdown in the production string. At this range of temperature and pressure between, for example, lines 260 and 258 in FIGURE 4A before they cross over, the injectants, especially those with higher carbon dioxide content, would be in the hydrate stability zone while the methane at this temperature and pressure is a vapor.

Control and Monitoring Subsystem

The gases and liquids in system 10 in FIGURE 1 are controlled and monitored by a control and monitoring subsystem. The control and monitoring subsystem includes flow control devices 78, 80, 82, and 84 that control the pressure (of the injectant and the

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produced gas) by means of valves, pumps, compressors, and/or expanders that control the temperature (of the injectant and the produced gas) by means of heaters, heat exchangers, and/or heat tape. Some of these devices, such as compressors, expanders, heaters or heat exchangers, may be part of the gas/injectant supply subsystem. The control and monitoring subsystem also includes sensing devices 86, 88, 90, and 92 that monitor pressure and temperature in the gas supply subsystem, the well subsystem for injection and production, and the subsurface containment subsystem. Conventional gauges (for example, either electrical or fiber optic) are used. The placement of these devices is such as to adequately monitor the production and injection strings in both the subsurface containment subsystem and elsewhere, such as in the gas processing modules 36, 40, 42 and 48. The injectant/gas circulation system is controlled and monitored to allow the initiation, the continuation, and the shutdown of circulation of an injectant and produced gasses. It is also utilized to optimize the rates of production of the gas and the rate of injection and the temperature of the injectant.

The Embodiment Shown in FIGURE 2

A more specific subsurface embodiment of the present invention is illustrated by the system 110 shown in FIGURE 2. System 110 includes several subsystems: a gas/injectant supply subsystem 112 that provides the gas/injectant; a well subsystem 114 that connects the gas/injectant supply subsystem to the in-place subterranean source of natural gas hydrates and that pipes the gas produced up to the surface; a subsurface containment subsystem 116 that provides gravity/density segregation of the liquid injectant which contains carbon dioxide, dissociation of the in-place methane hydrate, production of gas, and recycling of the injectant/gas provided by well subsystem 114 from gas/injectant supply subsystem 112; and, a control and monitoring subsystem that provides monitoring and control of the pressure, temperature, and composition and flow of the injectant and the produced gases.

Gas/Injectant Supply Subsystem

The gas/injectant supply subsystem 112 in FIGURE 2 employs one or more possible sources of gas for the injectant 118. For example, source 144 is a natural gas

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accumulation. Another example is exhaust 146 from a fossil fuel power generation plant 152. Another example is exhaust 148 from a fossil fuel compressor plant 154.

The gas from the above sources is compressed by compressor 150 into gas storage tank 120. The injectant 118 used for melting the hydrate is more efficient for heat transfer if the injectant is liquid at the zone where it is being injected; also more importantly if the injectant is liquid it allows for gravity/density separation of the liquid carbon dioxide injectant from the hydrate-evolved natural gas. Thus, the gas/injectant stream 118 is a liquid that is injected into the subsurface containment subsystem 116.

FIGURES 4A-F display several injectant compositions (containing different amounts of CO_2 and methane) where the injectant 118 contains at least some carbon dioxide. The shaded areas that are designated as shaded areas 250 and 252 in FIGURE 4A; shaded areas 300, 302, and 304 in FIGURE 4B; shaded areas 348 in FIGURE 4C; shaded areas 400 and 402 in FIGURE 4D; shaded areas 450 and 452 in FIGURE 4E; and shaded areas 500, 502, and 504 in FIGURE 4F show the pressures and temperatures where the liquid phase or critical phase of the injectant 118 is stable and the vapor phase of the hydrate 172 is stable and the injectant at subsurface conditions has a density greater than the density of the vapor phase released by the dissociation of the hydrate. The injectant 118 needs to be a liquid and to be denser than the vapor phase released during hydrate dissociation for the desired gravity/density partitioning to take place.

The optimal pressures and temperatures are designated as shaded area 252 in FIGURE 4A, shaded area 302 in FIGURE 4B, shaded area 402 in FIGURE 4D, shaded area 452 in FIGURE 4E, and shaded area 502 in FIGURE 4F.

The effects of injection pressure on formation fracturing in the subsurface containment subsystem will need to be evaluated on an individual well basis. The stability zone for hydrate occurrence and its exact pressure profile in the subsurface along with the pressure range under which fracturing will occur in the orientation of the fractures in this zone and its effects on the injection containment may further constrain the range of optimal pressure and temperature of the injectant. The shaded areas designated as shaded area 250 in FIGURE 4A, as shaded area 304 in FIGURE 4B,

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shaded area 348 in FIGURE 4C, shaded area 400 in FIGURE 4D, shaded area 450 in FIGURE 4E, and shaded area 500 in FIGURE 4F are at pressures that are above the fracture pressure of the rock formation containing the hydrate as well as the fracture pressure of the overlying shale. Injection at pressures greater than the fracture pressure can breach the subsurface containment. The stress fields at the time of injection are one factor critical to the orientation of the fracture (vertical or horizontal). A horizontal fracture does not pose a problem. A vertical fracture that fractures the overlying shale or subsurface containment may be a problem because of the migration of gas along that fracture and potential subsequent breach of containment and depressurization of injectant.

The shaded areas designated as area 300 in FIGURE 4B and area 504 in FIGURE 4F are not effective at partitioning the evolved natural gas from the hydrate because of the injectant vapor which is present in these pressure and temperature ranges.

The gas processing module 124 in FIGURE 2 performs gas processing functions such as expansion or compression, temperature control, water removal, and/or composition adjustment as is available from conventional technology of the industry. The gas/injectant 118 is then pumped down through conduit 122 in FIGURE 2.

Produced gas processing module 126 is on the surface and separates the components in the produced gas 136, such as methane and carbon dioxide, and removes water prior to sending the methane component 128 through pipe 130 to the production facility 132 and prior to re-circulating the carbon dioxide component 134 through pipe 142 to gas storage tank 120. Methane 138 from production facility 132 flows through pipe 140, as needed, to power generation plant 152 or to compressor plant 154. Gas processing modules 124, 126, and 150 may be part of the production facility or central compressor plant 132 and may contain common elements.

Well Subsystem

The well subsystem 114 includes the injection pipe string 122, the production pipe string 156, the larger well bore 158, injection packer 160, and production packer 162.

As explained above, the final injectant 118 flowing down the injection pipe string 122 can come from one or more possible sources 144, 146, and 148. The

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production pipe string 156 transports production gas 136 to the gas processing module 126.

The well subsystem is created by drilling and completing at least one well in a subterranean formation where there is at least some natural gas in the form of hydrate and the conditions are chosen where the formation and hydrate occurrence allows for a subsurface containment system.

FIGURE 2 shows the well bore 158 lined with conventional casing 164 which has been drilled in a subterranean formation in a pressure and temperature region so that well bore 158 penetrates a zone of hydrate. Cement 166 has been placed around the exterior of casing 164. The following effects need to be considered in the design of the well: (a) melting of the surrounding well bore hydrate and/or ice/ permafrost by heat transfer from the injectant or casing cement heat of formation; (b) casing strain and stress effects via changes in pore pressure because of different subterranean rock properties effecting ice or hydrate stability; and, (c) the formation of hydrates in the production and injection strings especially in times of shut down. The well should include the necessary precautions to remedy these effects. These remedies include insulated piping and casing, hydrate formation prevention techniques, hydrate inhibitors, heat tape, cement selection, and selection of slip joints as is available from conventional technology of the industry.

Boreholes are drilled at the desired distances and patterning from the surface into the subterranean formation. Thereafter the casing, cement, and piping are set into the formation to the desired depth. As shown in FIGURE 2, the lower portion of casing 164 and cement 166 are perforated or slotted over the zone of interest in the hydrate. The injection string is to be placed so that injection occurs at greater pressure and is placed deeper than the production string, production so that gravity segregation can occur. The completion is designed to promote injectant emplacement so that it is at the bottom of the well while dissociation of hydrate 172 can continue from heat transfer from the injectant and from depressurization from the production string 156, so that convective and conductive heat transfer and depressurization are optimized. The system may be employed in a horizontal well so long as the injection string is located so that the natural gas migrates into the production string via pressure differences. Since the system relies

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on gravity segregation, the injection string should penetrate deeper than the production string.

Subsurface Containment Subsystem

The subsurface containment subsystem 116 in FIGURE 2 includes natural geologic containment structure 168 comprised of a layer of shale 170 and the in-situ solid (unmelted) natural gas hydrates 172. The size of the zone (created by the dissociation of the hydrates) within geologic containment structure 168 will increase over time. For example, at time T1 the zone within the geologic containment structure will be of size 174; at time T2 the zone within the geologic containment structure will be of size 176; and at time T3 the zone within the geologic containment structure will be of size 178. Thus, this dynamic containment structure 168 will be defined through time by subsurface and injection conditions as the hydrate dissociation increases with time.

Injection packer 160 is placed in well bore 158 to block injectant 118 from production string 156. Production packer 162 is placed higher in well bore 158 to block production gas 136 from going up inside well bore 158 and to insure that production gas 136 goes up production pipe string 156. The layer of shale 170 functions as the top of the subsurface containment subsystem 116. The containment shale 170 provides a vertical seal for the produced gas evolved from the hydrates underlying the containment shale.

The selection of the formation of the subsurface containment system is critical. It is selected so that an overlying lithologic-permeability barrier isolates the hydrate zone below and so that the permeability barrier will not be significantly affected by melting of the hydrate. The overlying lithologic-permeability barrier should be of sufficient lateral and vertical extent to allow the gas/liquid circulation system to operate and the pressure and temperature to be maintained for the liquid injectant.

Dissociation of the natural gas hydrate occurs by circulating the injectant 118 within the subsurface containment subsystem 116 by using heat transfer from the injectant, pressure change, and rate of dissociation of natural gas hydrate to allow the natural gas hydrate to dissociate to free natural gas and to migrate to the production

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string 156. The natural gas hydrate dissociates to water and methane, respectively, in a ratio of about 8:1.

If the injectant 118 is injected at a high enough pressure, fractures in the subsurface rock formation will occur. The shaded areas designated as area 250 in FIGURE 4A, area 304 in FIGURE 4B, area 348 in FIGURE 4C, area 400 in FIGURE 4D, area 450 in FIGURE 4E, and area 500 in FIGURE 4F are at pressures that are above the fracture pressure of the rock, which will possibly result in breaching the subsurface containment.

The effects of injection pressure on the formation fracturing on the subsurface containment will need to be evaluated on an individual well basis. The stability zone for hydrate occurrence and its exact pressure profile in the subsurface, along with the pressure range under which fracturing will occur such that it affects subsurface containment in this zone, may further constrain these optimal pressure and temperature regions.

If the principal stress fields or perhaps other unknown factors are such that these fractures are parallel to the bedding and to the containment shale barrier at the top of the interval, there should not be a problem with vertically breaching the subsurface containment subsystem via fracture. However no matter what the type of fracture, vertical or horizontal, the injectant should not be injected at a high enough pressure to cause the subsurface containment system to be breached by a fracture that would cause insufficient pressure retention in the subsurface containment subsystem for the injectant to exist as a liquid phase. For example, if the injectant 118 or the hydrate-evolved natural gas 136 exhibits pressure leak-off because a vertical fracture penetrated the sealing shale at the top of the subsurface containment subsystem, then the injectant may depressurize and become vapor.

Control and Monitoring Subsystem

The gases and liquids in system 110 in FIGURE 2 are controlled and monitored by a control and monitoring subsystem. The control and monitoring subsystem includes flow control devices 184, 186, 188, and 190 that control the pressure by means of pumps, compressors, and/or expanders and that control the temperature by means of heaters, heat

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water. The water which is evolved segregates downwardly. The next zone 234 is a hydrate melting zone where the hydrate is in the early stages of melting. The methane which is released flows upwardly. The water which is evolved flows downwardly.

In the zone above boundary 218 in FIGURE 3, clastic grains 220 are surrounded by hydrate filled pores 222. The amount of hydrate in the pores have been measured to be greater than 80 volume %. The exact location of the hydrate in pores 222, that is, whether the hydrate coats grains 220 or is located in the center of the pores, is not known.

In hydrate melting zone 234, pores 224 contains partially dissociated hydrate. As the hydrate dissociates, it releases gas and water so the remainder of pores 224 consist of water and methane gas. In hydrate melting zone 232, the evolved and in-place water in pores 226 separates from the methane gas evolved from the hydrate. In mixing zone 230, water and the liquid injectant mix in pores 228. In this zone 230, pores 228 are now devoid of any hydrate.

As the hydrate is heated or depressurized, water and methane gas evolve at an approximate 8 to 1 ratio in the pore system. The methane gas separates from the water and the density difference supports the gravity/density separation of the hydrate-evolved natural gas from the water. The hydrate evolved natural gas is nearly 100% methane. The methane gas migrates upwardly because of its significantly lower density compared to water and the liquid injectant. Because of the 8:1 ratio of water to gas in the melting of the hydrate, there is expected to be significant retardation of mixing the hydrate-evolved natural gas and the injectant resulting in only minor mixing of the evolved natural gas with the injectant. Some mixing of the carbon dioxide injectant and the methane may occur, resulting in a mixed natural gas containing methane and carbon dioxide gas as well as the liquid injectant becoming more methane rich. As can be seen from the phase diagrams, the more methane in the injectant the higher the pressure and temperature required for the liquid phase to exist. Methane is produced before it is allowed to mix with the injectant.

In the case where a free gas zone exists below the hydrate, the initial subsurface containment subsystem can comprise the container holding the free gas. This free gas zone below the hydrate should be produced of any natural gas prior to supplying the

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hydrate zone with liquid injectant containing in part carbon dioxide. Maintenance of a higher pressure than the original pressure in the free gas zone may not be possible, so maintaining a pressure sufficient for the stability of the liquid injectant may be difficult in the free gas zone.

The presence of hydrate can restrict flow to the effect that hydrate filled pores are an effective permeability barrier and pressure barrier. Well test results of hydrate zones and spontaneous potential (SP) electric logs give support to this notion. Since the hydrate filled pore location changes with time and with dissociation of the hydrate, there is a dynamic change in the dissociation zone and in the convective paths possible for injectant circulation as shown as in FIGURE 1 at 70, 72, and 74 which represent the changes occurring at times T1, T2, and T3, respectively.

Field studies and reservoir modeling results suggest that circulation through a free gas zone that often lies below the base of hydrate zones should allow convective and conductive recovery of in-place hydrates. Since free gas zones do not necessarily occur in all hydrate reservoirs, utilization of completion technology and well bore technology (such as horizontal wells) are optimized to set a path of circulation that leads to convective flow of the injectant. This is done by placing the injector near to the base of the hydrate zone or in the free gas zone so that convection can occur as the hydrate dissociates and in the already dissociated hydrate zones.

Fracturing of the subsurface structure is a possible way to enhance the convective circulation of the injectant. This would aid in developing a good injectant circulation pattern. If vertical fractures develop, care must be taken not to breach the shale barrier that forms the upper seal for the subsurface containment subsystem. Horizontal fractures may be very effective at enhancing convective circulation; however, horizontal fracturing typically occurs in areas where the principal stress directions are such that the vertical principal stress is less than either or both of the horizontal principal stresses.

Heat transfer from the circulating injectant is both convective and conductive and the design of the subsurface containment subsystem and the well subsystem completions should optimize convective flow and density segregation of the liberated methane gas

exchangers, and/or heat tape. The control and monitoring subsystem for the subsurface includes sensing devices 192, 194, and 196 that monitor pressure and temperature in the gas/injectant supply subsystem, the well subsystem for injection and production, and the subsurface containment subsystem. Conventional gauges (for example, either electrical or fiber optic) are used. The gas circulation system is controlled and monitored to allow the initiation, the continuation, and the shutdown of circulation of gases for injection and production.

Permeability of the pore system

Permeability of the pore system with hydrate and dissociated hydrate are critical to setting up circulation of the injectant stream. The injectant circulation stream transfers heat by conduction and convection. The hydrate will be dissociated by this heat in addition to depressurization. By convection the circulation of the injectant stream can better dissociate the hydrate. FIGURE 3 is a magnified schematic representation of the pore system 210 in its relationship to permeability with evolution from a solid hydrate to gas.

FIGURE 3 illustrates the phases in the process of dissociation that the methane hydrate experiences. In pore system 210, above boundary 218 is a zone where the frozen hydrate in the pore system is not yet changed. This zone forms a pressure and permeability barrier to fluid flow. In conjunction with the overlying shale barrier, this zone above boundary 218 forms the subsurface containment subsystems in FIGURES 1 and 2. Boundary 218 is a dynamic boundary moving with time. At earlier points in time, the boundary was at location 216, at location 214, and at location 212. It will be understood that in reality the boundary moves continuously, rather than by moving in the discrete changes illustrated in FIGURE 3.

In addition to the solid zone residing outside of boundary 218, FIGURE 3 also illustrates zones 230, 232, and 234. Zone 230 is a mixing zone where the liquid injectant mixes with water that has evolved from the hydrate. In this zone 230, the injectant is transferring heat by convection and by conduction. The next zone 232 is a hydrate melting zone where the hydrate is in the final stages of melting. The methane which is released flows upwardly because of gravity segregation/density differences with the

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carbon dioxide to increase the carbon dioxide content to 50.00 mole %. At this mixture of gas cap gas and carbon dioxide, the injectant forms a liquid that is below fracture gradient. Although testing of whether the fractures formed above fracture gradient are vertical or horizontal is needed to determine if fractures would breach the subsurface containment. Field tests are needed to verify the fracture gradient.

FIGURES 5A and B are pressure and temperature diagrams that show:

1. The phase diagram and envelope (lines 560 and 612) of an injectant where the injectant is of the specified composition, the phases of the injectant that have a liquid phase (or critical phase) and are shaded for three conditions where methane vapor exists:

(a) The liquid and vapor phase of the injectant co-exist and the injectant has a density greater than the vapor released upon dissociation of the hydrate (areas 550 and 600);

(b) The liquid phase of the injectant exists (that is, there is no vapor phase of the injectant) or the critical phase of the injectant exists and the injectant has a density greater than the vapor released upon dissociation of the hydrate and the pressure is below the fracture pressure gradient (area 602); and

(c) The pressure is above the fracture pressure gradient (areas 552 and 604).

2. The phase envelope (lines 558 and 610) for 100% methane. For this phase envelope, the hydrate phase is in the higher pressure and lower temperature region and the vapor phase is in either the lower pressure or higher temperature regions. The typical composition of an in-place hydrate is near 100% methane.

3. The specific temperature and pressure profile of a well (lines 556 and 608) within the area of hydrate occurrence. This is the temperature and pressure profile for each well. The intersection of the well bore pressure and temperature gradient (lines 556 and 608) with the methane phase envelope (lines 558 and 610) shows where the in-place hydrates are stable and can exist in the subsurface.

4. The fracture gradient for the well (lines 554 and 606) is the injection pressure which, if exceeded, will fracture the formation. The fracture pressure of a well, where hydrates are stable, depends on the depth of the hydrates. The maximum fracture

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pressure is based upon the maximum depth of the hydrate occurrence. Fractures can breach the subsurface containment and cause pressure leak off. Vertical fractures can leak off to low pressure zones. Whether vertical fractures occur is dependent on local stress conditions or perhaps other factors. Horizontal fractures may even help the production process. The area shaded 552 and 604 can contain non-liquid injectant.

For the pressure and temperature profiles for the arctic-permafrost setting, a pressure gradient of 0.421 psi/ft and a fracture gradient of 0.695 psi/ft were used. For the pressure gradient for the marine-continental shelf setting, a pressure gradient of 0.45 psi/ft and a fracture gradient of 0.695 psi/ft were used. Temperature gradients were taken from T.S. Collett et al., "Natural Gas Hydrates", SPE-AAPG Western Region Meeting, May 23, 2002, Anchorage, Alaska. Fracture gradients, well bore pressures, and temperature gradients are dependent on the conditions specific to the location of the well.

It should be noted that if the injectant is above the critical point of the injectant, the injectant is a single phase. For pure carbon dioxide, a temperature 87.87° F, a pressure of 1071 psia and a volume 0.0342 cu ft/lbm. constitute the critical point (see Robert S. Metcalf, Petroleum Engineers Handbook, Table 20.2 Some Physical Constants of Hydrocarbons). At conditions such as these, the injectant has the characteristics of a single phase. This critical phase can be used as a liquid injectant if the density is greater than the vapor released from the hydrate at subsurface conditions. Phase and density data specific to the injectant and to the in-place hydrate composition where this invention is to be used should be obtained from laboratory analyses to ensure that the appropriate relationships between pressure, temperature, and density for the injectant are used in the inventive system.

The gas cap in the Prudhoe Bay Unit (PBU)

The gas cap in the PBU contains 23 TCF (trillion cubic feet) of gas containing 13 mole % CO_2. Separating this carbon dioxide, then injecting the carbon dioxide into the Eileen hydrate to produce methane, and sequestering the carbon dioxide there would significantly reduce the amount of greenhouse gases being released into the atmosphere and at the same time would produce large amounts of methane. There exists over 400 TCF of hydrates located under the North Slope of Alaska.

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The current proposal to exploit the gas cap in the PBU is to construct a gas pipeline connecting the North Slope to the lower 48 states' gas pipeline grid. The lower 48 states' gas pipeline grid would then supply the methane to electric power plants in the lower 48 states where the carbon dioxide (created by burning the methane in the electric power plants) could not or would not be sequestered (i.e., the carbon dioxide would be released into the atmosphere). In this plan, the methane from hydrate production can be used to offset costs associated with the gas removal of CO_2 of the PBU gas and provide natural gas with less requirements for carbon dioxide removal. The clean up of the gas is expected to range from $1.5-2.0 Billion.

My better plan is to exploit the gas cap in the PBU by using the gas to generate electric power at the North Slope of Alaska and to construct electric power lines (such as high voltage direct current (HVDC) lines) connecting to the lower 48 states' power grid. My plan would be implemented instead of constructing the proposed gas pipeline connecting the North Slope to the lower 48 states' gas pipeline grid. Under my plan, the carbon dioxide produced by burning the methane in the electric power plants would be captured and then injected into the Eileen hydrate to produce methane. The carbon dioxide would be sequestered there, significantly reducing the amount of greenhouse gases being released into the atmosphere and at the same time producing large amounts of methane.

Many of the lower 48 states' power plants are older and release significant amounts of carbon dioxide into the atmosphere. A large number of new electric power plants are envisioned to use this gas from the proposed North Slope pipeline. The U.S. Department of Energy's Solid State Energy Conversion Alliance (SECA) suggests that new electric power generation technologies will result in a considerable reduction in the cost of electric power generation and that these new technologies will be available in the near term (within five years).

Thus, instead of building the proposed new gas pipeline and a large number of new electric power plants in the lower 48 states, my better plan is to build the new electric power plants in Alaska on the North Slope in order to utilize the North Slope gas.

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At the same time, my plan would sequester the carbon dioxide produced by the power plants while producing more methane from the in-place hydrates.

Some of the new electric power generation technologies, such as fuel cells, not only produce less carbon dioxide and NO_X but also can run on fuels containing carbon dioxide and the products are electricity, heat, and carbon dioxide. Instead of expanding the U.S. contribution of carbon dioxide to the atmosphere, my plan would capture the carbon dioxide and use it to produce methane from the hydrate deposits that were not previously economical to exploit. The net result of my plan is to provide electric power at a lower cost.

By locating the power plants where hydrates exist, the carbon dioxide produced from power production could be injected into the hydrate zones. If it is assumed that 2.5-6.5 BCF (billion cubic feet) of natural gas per day would be sent through the proposed pipeline, then a significant percentage (preliminary estimates of 30-100%) of the carbon dioxide that the U.S. produces in excess of the baseline for the Kyoto accord could be injected and sequestered from the atmosphere and used to produce some of 400 TCF of methane gas that exists in hydrates under the North Slope of Alaska. Currently methane production in the US has stabilized from prior declines because of coal bed methane and deep gas sources but no net production increase exists; the question of whether new resources can be developed to account for the production decline from natural gas reservoirs within the US is critical to US energy policy.

While the preferred embodiments of the invention have been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention. While the preferred embodiment of the invention has been illustrated and described, as noted above, many changes can be made without departing from the spirit and scope of the invention. Accordingly, the scope of the invention is not limited by the disclosure of the preferred embodiment. Instead, the invention should be determined entirely by reference to the claims that follow.

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from the liquid phases of injectant based on the choice of the location of the production and injection strings/wells in the subsurface.

The nearer the injectant pressure and temperature is located on the pressure-temperature diagram to the phase boundary of the solid in–place hydrate the lower the requirement of heat needed to melt the hydrate. Higher pressure and temperature for the injectant increase the costs of the injectant. This should be taken in to account in design of the temperature and pressure at which injection occurs.

FIGURES 4A-F are diagrammatically constructed using the program CSMHYD.exe developed by E. D. Sloan, Jr. and the trend of the carbon dioxide vapor and liquid phases of carbon dioxide. The phase areas shown beyond the phase boundary for hydrate formation are only diagrammatic displayed and may not represent the true phase boundary. These phase diagrams are shown for illustration only and need to be developed from laboratory tests for each hydrate accumulation and for each injectant. It is recommended that laboratory tests be performed to confirm the phase boundaries and density data for the injectant that will be used.

Injection in the proper pressure and temperature range is accomplished by the system of monitors and controls. At the end of useful methane hydrate production, the pressure and temperature of the production well may be reduced to a temperature and pressure range that would allow the in-reservoir injectant to form a hydrate.

The production natural gas that has circulated to the production string may be cyclic. The rate at which methane evolves and segregates is critical to the production cycle. Production from time to time may be shut in or sent to gas storage so that the optimal flow of methane rich gases can be sent to the production facility.

Gravity/density segregation of the liquid injectant and the water from the natural gas evolved from the in-place hydrate allows most of the carbon dioxide in the injectant to remain in the subsurface. The density-segregated natural gas is produced to the surface where it is processed in the production facility to further to remove methane which is distributed to a pipeline or utilized locally for power production or compression. Any carbon dioxide removed from the natural gas in the processing facility is cycled back to the subsurface. Changes in the pressure and temperature of the injectant and water

mixture in the subsurface proceed to conditions where a clathrate of carbon dioxide is formed in the subsurface, thus leaving carbon dioxide not only sequestered, but sequestered as a hydrate.

The produced natural gas may be further processed before being supplied to the gas supply subsystem, since the produced natural gas may contain both methane and carbon dioxide. The injectant that is retained in the subsurface containment subsystem as a liquid or hydrate results a decrease of the overall percent of carbon dioxide vented to the atmosphere and sequestration of carbon dioxide in the subsurface is the result.

Example

Prudhoe Bay's Eileen Hydrate Accumulation

As stated earlier, in the Prudhoe Bay Reservoir, Alaska, the natural gas accumulation is beneath the hydrate zone known as the Eileen Hydrate Accumulation. This natural gas accumulation is called the Prudhoe Bay Unit (PBU) gas cap. The hydrate accumulation that overlies the PBU gas cap could be developed from (1) the carbon dioxide that exists in the PBU gas cap or (2) methane in the PBU gas cap could be utilized for power generation and the effluent carbon dioxide captured and employed to produce the hydrates.

The composition of the hydrate in the Eileen accumulation is nearly 100% methane. As shown above, the PBU gas cap contains about 13 mole % carbon dioxide. Separation of this carbon dioxide is needed before pipeline shipping of the methane. This captured carbon dioxide could be used to produce the hydrates located above the PBU gas cap.

FIGURE 5A shows the phase relationships that exist for an injectant (containing only about 13 mole % carbon dioxide) formed directly from the PBU gas cap. Thus, FIGURE 5A is a phase diagram where the composition of the injectant is 75.02 mole % methane, 7.95 mole % ethane, 3.99 mole % propane, and 13.04 mole % carbon dioxide. This is the natural composition of the gas cap that exists in the PBU.

FIGURE 5B is a phase diagram where the composition of the injectant is 43.13 mole % methane, 4.57 mole % ethane, 2.29 mole % propane, and 50.00 mole % carbon dioxide. This is the Prudhoe Bay gas cap composition with sufficient added

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